Optical characterizations of multi-shape nanoparticles in polymer thin film layers

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ABSTRACT

Recent progress in nanoparticle production gave a boost to nanotechnologies. Differently shaped and sized nanoparticles are produced by chemical synthesis in mild conditions. Nanoparticles have the potential to revolution the control of light matter interaction phenomena, thanks to their material, size, shape and environment dependence.

In the search for a perfect absorber in the visible wavelength, silver nanospheres, nanoprisms and nanocubes are synthesized and successfully embedded in a thin film layer. Optical characterizations are coupled to FDTD simulations to analyze the optical behavior of the embedded nanoparticles.

Each nanoparticle size and shape has a specific optical signature, which are modified by coupling phenomena between the nanoparticles. Optical properties of thin film layers containing nanoparticles are affected by the material, size, shape of the nanoparticles and their spatial distribution in the thin film layer.

Keywords: silver nanoparticles, PVP, heterogeneous thin film layers, optical properties, FDTD

1 INTRODUCTION

Since Faraday's systematic study of gold nanoparticles, tremendous research has been done in various scientific domains to take advantage of the extraordinary properties of nanoparticles. Progress in chemistry has lead syntheses of differently sized and shaped nanoparticles, for applications in various fields such as solar cells, catalysis, imaging or clinical treatment.

The optical properties of plasmonic nanoparticles are material, size, shape and environment dependent due to localized surface plasmon resonances. Noble metal nanoparticles interact strongly with the visible wavelength range. Among noble metals, silver nanoparticles exhibit the highest electric field enhancements, leading to interesting optical properties at lower nanoparticle densities in the visible wavelength range.

Our work focuses on the need to control the absorption of light in the visible wavelength range for military applications as stealth technologies and photodetectors, and for solar energy harvesting as well in photovoltaic cells as in thermal solar cells. Taking advantage of the size and shape dependence of silver nanoparticles, we aim to selectively absorb light by using different nanoparticles as nanospheres, nancubes and nanoprisms.

The nanoparticles are produced by wet-chemistry process in mild conditions. The nanoparticles are then embedded in a transparent and non-absorbing host matrix. The thin film layers are optically studied and the results are confronted with finite difference time domain (FDTD) simulations.

2 SAMPLE PREPARATION

In a first step the nanoparticles are synthesized. Then the colloidal solutions are mixed with the polymer solution to be deposited by spin coating on a clean substrate.

2.1 Chemical synthesis

Wet chemistry synthesis typically yields high concentration of nanoparticles with a small size disparity. It is also supposed to have potential for industrial production.
Nanospheres are produced in a single step silver ions reduction by sodium borohydride in water [1]. The nanospheres measure about 10 nm.
Nanoprisms are produced by a two step seed based method in water [2]. Spherical seeds with crystallographic defects are produced in a first step. In the second step, the added silver binds preferentially to the defects leading to a lateral growth and by extend to nanoprisms. The quantity of seed solution used in the second step of the synthesis determines the size of the resulting nanoprisms. The nanoprisms measure about 30 up to 100 nm edge size with a constant thickness of about 10 nm due to the growth mechanism. The colloidal solutions of nanoprisms cover the whole visible wavelength range.

Nanocubes are produced by a polyol process in ethylenglycol [3]. The nanocubes measure about 35 nm edge length.

2.2 Polymer host matrix

The polymer host matrix is chosen to be transparent and non-absorbing in the visible wavelength. Furthermore, the compatibility with the silver nanoparticles has to be high to avoid rounding of the nanoprisms' and nanocubes' corners. Polyvinylpyrrolidone (PVP) is identified as an excellent host matrix and surfactant. Furthermore, it is soluble in water and in ethanol.

The PVP solution is then mixed together with the colloidal solution to be deposited.

2.3 Thin film layer deposition

The mixed solution is deposited by spin coating on previously cleaned substrates. Spin coating deposits thin film layers of a few tens of nanometers up to 1 micrometer, following the rotation speed and time.

3 OPTICAL CHARACTERIZATIONS

The optical properties of the thin film layers are measured by spectrophotometer and spectroscopic ellipsometry to have complementary information, i.e. the reflectance and transmittance intensities of each sample and the complex refractive index respectively.

3.1 Nanospheres in PVP

Nanospheres in PVP display a unique dipolar absorption peak around 409 nm. The measured diffuse reflectance is low, which is consistent with the Mie theory calculations for silver nanospheres of 10 nm.

3.2 Nanoprisms in PVP

Originating from their more complex geometry, nanoprisms display several absorption peaks. The highest intensity absorption peak is the in-plane dipolar absorption. For synthesized nanoprisms of about 50 nm edge size in PVP, the in-plane dipolar absorption peak is centered around 690 nm. The second peak centered around 440 nm is identified at the in-plane quadrupolar peak. It should be noted, that several steps of centrifugation of the colloidal solution are necessary to separate the produced nanoprisms from the residual spheres.

Nanoprisms of edge size between 30 and 100 nm are produced by the chemical synthesis chosen. The in-plane dipolar absorption peak is shifted from 450 nm up to 900 nm when deposited in PVP.

3.3 Nanocubes in PVP

The nanocubes display a strong absorption peak centered at 428 nm and a shoulder around 506 nm. The strongest absorption peak is associated to the dipolar resonance of the nanocubes.

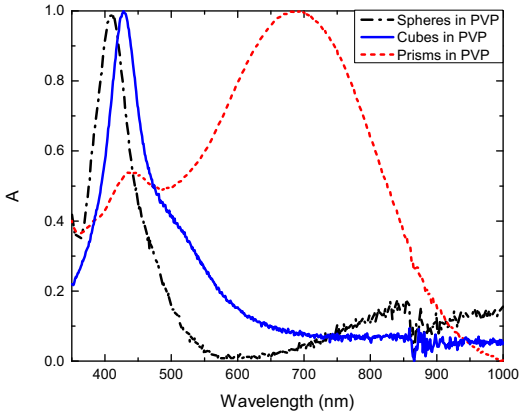

Figure 1: Normalized absorption of nanospheres, nanocubes and nanoprisms embedded in PVP thin film layers.

4 FDTD SIMULATIONS

FDTD simulations are performed under the commercially available software Lumerical [4]. In a first step the nanoparticle alone is studied to evaluate its intrinsic optical properties. The absorption and scattering cross sections are calculated for every synthesized nanoparticle size and shape using. The main drawback of chemical syntheses is the size disparity of the produced nanoparticles. This is taken into account by calculating the cross sections for several sizes. Furthermore, sharp edges are not energetically favorable. The edges are rounded, even with in presence of a surfactant. Rounded corners are taken into account in our calculations. It must be noted, that the electric field enhancement, normally located at the sharp tips the nanoprisms and nanocubes, is spread on a larger surface [5].

If the measured optical properties are similar to the calculated properties of single nanoparticles, it is concluded that the nanoparticles do not interact, i.e. there is no coupling between the particles. This is observed for low densities of nanoparticles. For higher densities of nanoparticles, coupling and aggregation phenomena have to be taken into account. This is achieved by simulating coupled nanoparticles, as shown in Figure 2, or touching nanoparticles [6].

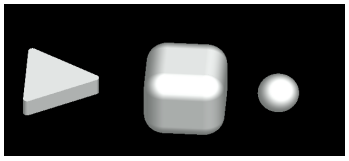

Figure 2: Nanoprism, nanocube and nanosphere in close proximity.

Figure 3 displays the extinction cross section, i.e. the addition of the absorption cross section and the scattering cross section, of a single nanosphere, a nanoprism and a nanocube array in PVP, as shown in Figure 2. The cross sections are calculated for an electromagnetic wave arriving perpendicular to the nanoprism and nanocube surface for s and p polarization. The out-of-plane peaks from the nanoprism are not taken into account because of their low intensity.

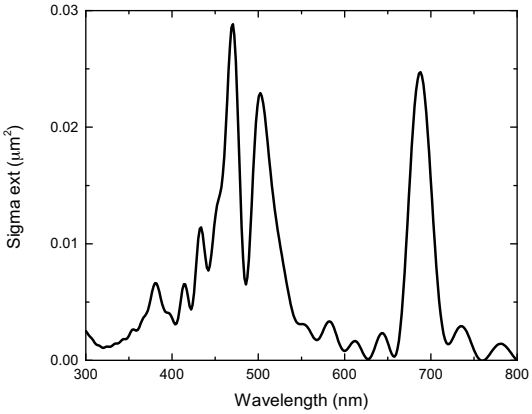

Figure 3: Calculated extinction cross section for three different silver nanoparticles in PVP.

The extinction peak around 700 nm is associated to the nanoprism dipolar resonance. The peak around 500 nm is associated to the dipolar resonance of the nanocube and the peak around 430 nm is associated to the nanosphere. The coupling between the particles is translated into a redshift of the different peaks when compared to the extinction peaks of the nanoparticles alone in PVP.

CONCLUSIONS

In summary, we synthetized silver nanospheres, nanoprisms and nanocubes by wet chemistry methods. The nanoparticles are deposited in a non-absorbing host matrix to control the absorption of the thin film layer.

FDTD simulations verify the optical properties of the nanoparticles in the thin film layers. Calculations for nanosphere, nanoprisms and nanocubes in the same host matrix show promising results.

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